Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 104 (2005) 55–63

CATALYSIS TODAY

www.elsevier.com/locate/cattod

# Advanced catalyst technology and applications for high quality fuels and lubricants

Michael C. Kerby [*], Thomas F. Degnan Jr., David O. Marler, Jeffrey S. Beck

*ExxonMobil Research and Engineering, Annandale, NJ 08801, USA*

## Abstract

Within the petroleum refining and petrochemical industries, catalysts provide the opportunity for drop-in solutions for addressing ever more stringent product quality and environmental specifications. Improved catalysts have also been instrumental in debottlenecking many refining and chemical processes. In order to stay competitive, many companies are focused on taking advantage of higher activity and more selective catalysts to facilitate ‘‘capacity creep’’. Increasingly, these catalyst advances stem from the commitment to develop and nurture active materials platforms. ExxonMobil has focused its platform efforts in several areas including micro- and mesoporous molecular sieves, supported metals, and mixed metal oxides and sulfides. The recently announced alliance between ExxonMobil and Symyx Technologies, Inc. (Santa Clara, CA) is a further step in the company’s commitment to strengthen its materials platforms.

*Keywords:* Catalysis; Zeolites; Clean fuels

## 1. Introduction

The global refining and petrochemical industries face increasingly more difficult technical challenges. Stricter environmental mandates and more demanding product quality specifications contrast with an operational environment structured around processing heavier and more contaminant-laden crudes on the refining side and ‘‘opportunistic’’ feeds containing more byproducts on the chemicals side. Frequently, the most cost effective and efficient way to confront these challenges is through implementation of newer catalyst technology [1]. This paper describes how ExxonMobil is exploiting its catalyst technology ‘‘pipeline’’ as catalytic materials move from discovery to development and ultimately to deployment. ExxonMobil is focused on reducing the often lengthy interval between discovery to deployment by using a range of strategies, many of which are linked to high throughput experimentation and closely associated model development.

Nearly, 90% of all molecules in crude feedstocks eventually find their way into contacting a catalyst of some sort. The majority of major refining conversion processes are catalytic, the exceptions being thermal conversion processes such as delayed or fluid coking and visbreaking. While catalysts accelerate desired reactions they also lower energy requirements. Catalysts provide a focal point for improving plant energy efficiency and debottlenecking operations. The US refining industry has been exceptionally successful in using both catalysts and process engineering to expand refining capacity while minimizing capital investment. In fact, there have been no new refineries constructed in the United States since 1978 [2]. Between 1980 and 2002, the industry shut down 160 of its 319 domestic petroleum refineries, yet refining capacity remained constant at approximately 18 million barrels per day [3]. Increasingly, the refining and petrochemical industries have come to rely on a steady record of catalytic advances to increase plant efficiency. Catalyst advances improve the flexibility for units to squeeze more value from existing hardware while meeting the tighter molecular specifications required of today’s fuels, lubricants, and petrochemicals. Catalysts are also a major operational expense. ExxonMobil annually purchases more than 100 million lb of catalysts for its refineries and petrochemical plants.

---

[*] Corresponding author. Tel.: +1 908 730 2116; fax: +1 908 730 3031.
*E-mail address:* michael.c.kerby@exxonmobil.com (M.C. Kerby).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.03.028

## 2. Catalytic challenges

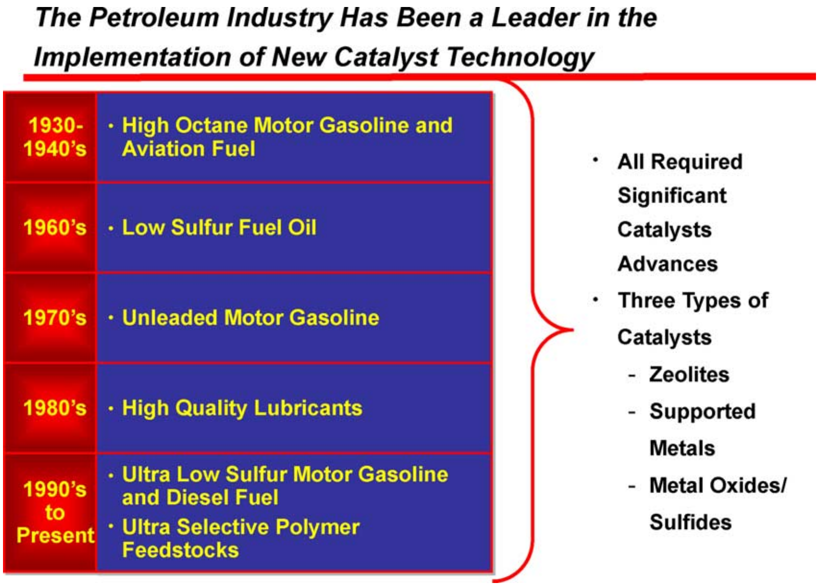
In transportation fuels, the focus is on improving both product yields and product quality. The term quality also extends to removal of nitrogen and sulfur compounds from fuel products, mainly for environmental reasons. In lubricants, the market is demanding better viscometrics—improved viscosity retention (i.e., higher viscosity indices) and lower pour points. This translates into more highly hydroprocessed stocks, which contain predominantly branched paraffins. Finally, in the area of commodity petrochemicals, the focus is on higher selectivity principally in the production of aromatics and olefins.

Petroleum companies, and particularly ExxonMobil, have been major innovators in the development and adaptation of new catalytic technologies (Fig. 1). In the 1930s and 1940s, the build-up to the war efforts provided the incentive for the development of fluid catalytic cracking catalysts and with them the production of higher performance motor and aviation gasoline. In the 1960s, hydroprocessing became viewed as a practical means of improving fuel quality, and advanced supported metal catalysts began to emerge. The 1970s brought oil supply disruptions and the phase-out of lead from gasoline. This spawned catalytic research in the areas of synthetic fuels, e.g., methanol to gasoline and Fischer Tropsch synthesis, as well as reforming and FCC catalysis oriented toward producing more aromatic- and olefin-rich gasoline to supplant the octane lost through the phase out of tetraethyl lead. Sulfur reduction in gasoline and specialty petrochemicals were focal points in the1980s and 1990s, and the petroleum industry responded with a slate of highly tailored and specific shape selective catalysts oriented toward higher quality and lower operating cost. Advances in catalyst design and development have required improved understanding of how to discover new materials, develop them into active materials, and commercialize them at a reasonable cost. Zeolites, supported metals, and mixed metal oxides/sulfides are the three types of catalysts that have been, over a sustained period, the source of most major advances in refining and petrochemical catalysts. The ability to exploit these materials has increasingly relied upon a better understanding of how molecular sieve, metals, and mixed metal oxide/sulfide catalysts behave at the molecular level.

## 3. ExxonMobil's active materials platforms

ExxonMobil is developing next generation catalyst ‘‘platforms’’ that will support future business needs. In addition to zeolites and supported metals, the company's other major heterogeneous catalyst platforms include mixed metal oxides/sulfides and mesoporous materials (Fig. 2). The company relies on these platforms for advanced catalyst developments to maintain the operational flexibility it needs to improve its products and often to provide ‘‘drop-in’’ solutions to tighter environmental regulations. The capabilities in these platforms extends throughout the technology pipeline (Fig. 3), from discovery through development and into commercial deployment.

The discovery component includes the use of strong fundamental science in identifying promising new structures and compositions. Detailed screening involves analysis of intrinsic kinetics combined with kinetic modeling of model compound reactions, and advanced materials characterization. A thorough understanding of catalytic hydrocarbon chemistry is combined with a computational analysis of the active site and the transition state to identify the best candidates.



**The Petroleum Industry Has Been a Leader in the Implementation of New Catalyst Technology**

| | |
|---|---|
| 1930-1940's | · High Octane Motor Gasoline and Aviation Fuel |
| 1960's | · Low Sulfur Fuel Oil |
| 1970's | · Unleaded Motor Gasoline |
| 1980's | · High Quality Lubricants |
| 1990's to Present | · Ultra Low Sulfur Motor Gasoline and Diesel Fuel<br>· Ultra Selective Polymer Feedstocks |

- All Required Significant Catalysts Advances
- Three Types of Catalysts
  - Zeolites
  - Supported Metals
  - Metal Oxides/ Sulfides

Fig. 1. The petroleum industry has been a leader in the implementation of new catalyst technology.

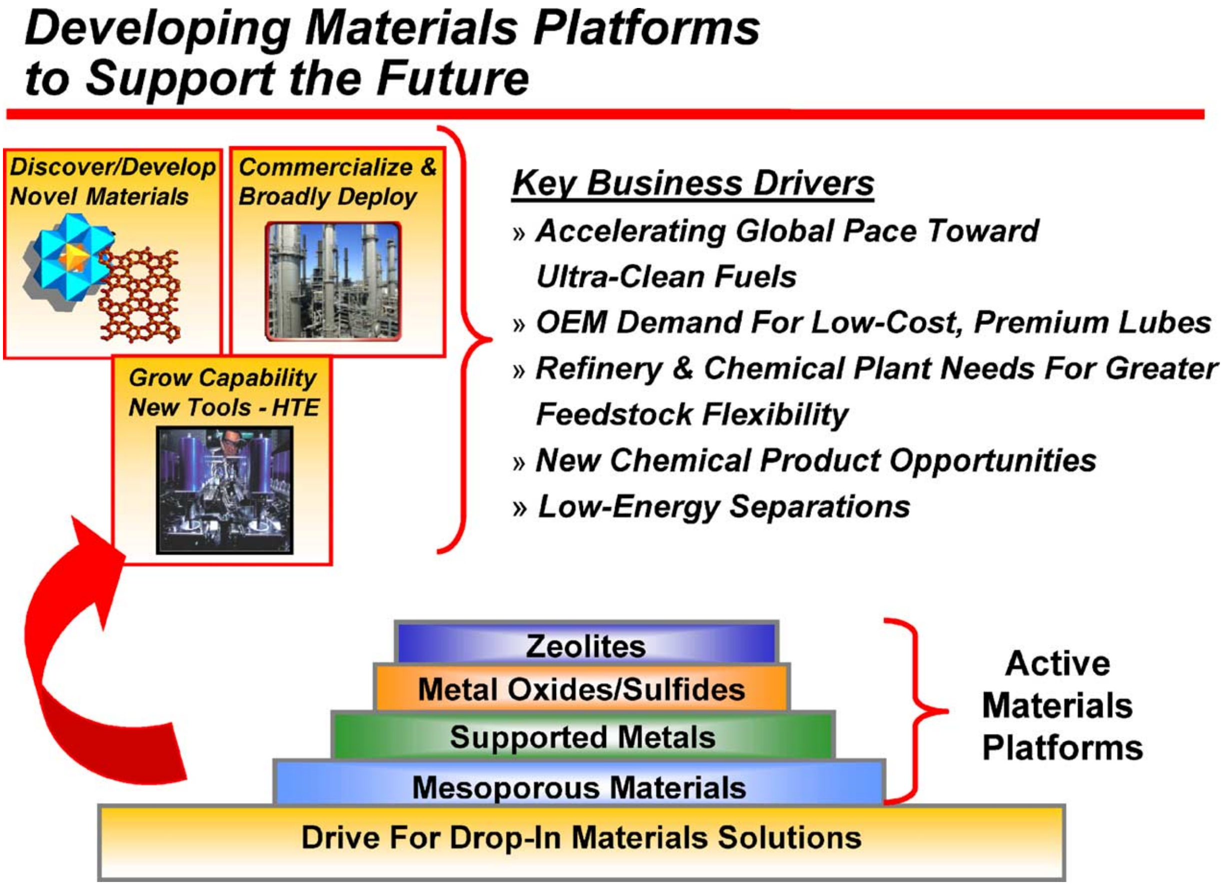


Fig. 2. Developing materials platforms to support the future.

Development involves an iterative refinement of catalyst properties using carefully planned catalytic tests. Once the preferred formulation is identified, work starts on finding the most cost effective means to manufacture the catalyst. Development is carried out at a scale that increases confidence of successful commercialization. The development stage normally takes the catalyst formulation from the gram scale to the 10–100 kg scale. The decision whether to internally manufacture the catalyst, collaborate with another company to co-develop the catalyst, or simply to toll manufacture the catalyst involves the consideration of a large number of factors including cost, strength, and breadth of intellectual property coverage, compatibility with internal manufacturing capabilities, and even geographical proximity to base research and development operations. Once the commercial catalyst is produced and a representative composite sample is obtained, the final steps in establishing the process yields and selectivity can be completed. Lastly, but most importantly, the catalyst is deployed as broadly as possible. The process data from the commercial units provide valuable information about catalyst durability and longevity and ultimately validate the scale-up work. In sum, designing a catalyst is just as complex as designing a computer chip. Just as a computer chip manipulates information in its final form, a well-designed catalyst transform molecules into their final form, rapidly, efficiently, and with high selectivity.

## 4. Exxon and Mobil—a marriage of catalytic science and material strengths

Prior to the merger of Exxon and Mobil in December 1999, both companies had strong, yet complementary catalytic materials capabilities. Exxon brought a history of excellence in supported metal and mixed metal catalysts along with a strong effort in large pore, highly acidic molecular sieves. Just as importantly, Exxon scientists had long studied and had developed a deep understanding of acidity in solids and metal-support interactions. Mobil brought a rich heritage in the discovery of new materials, particularly micro- and mesoporous molecular sieves along with a sound understanding of silica chemistry, shape-selectivity, and an internal capability for materials scale-up and commercial manufacture.

Today the focus is on strengthening all platform areas and on exploiting opportunities at the interfaces to address a set of technical challenges that include:

- lower targets for sulfur and nitrogen in gasoline and diesel;
- lower cost, higher performance lubricants;
- heavier and more aromatic hydrocarbon feed streams;
- greater versatility and process flexibility in producing olefins and aromatics;

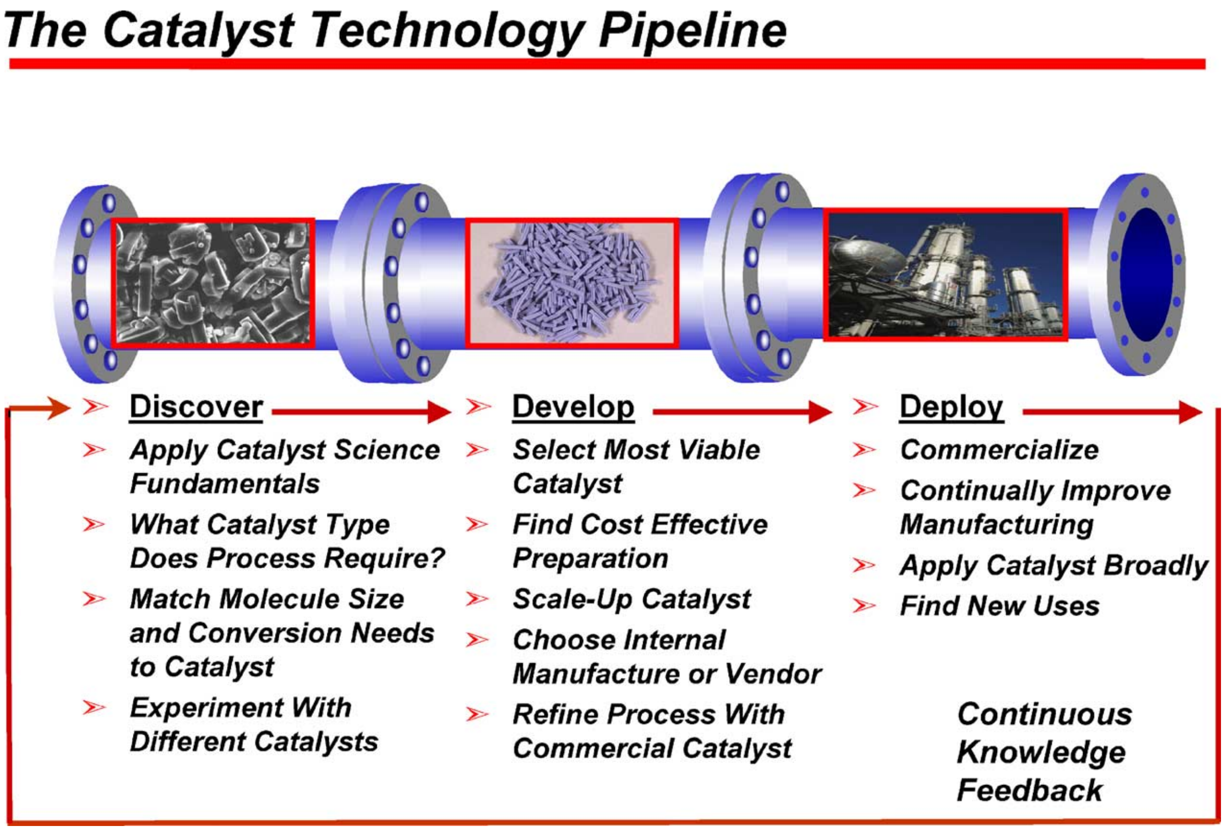


Fig. 3. The catalyst technology pipeline.

- new petrochemical opportunities;
- low energy separations that focus on efficient molecularly specific segregation.

To avoid bottlenecks, emphasis has to be placed on developing capabilities throughout the materials pipeline from discovery through development of new materials all the way to commercial deployment. There is significant value in reducing time and complexity of each part of the materials pipeline. Accelerating the pace of discovery provides earlier and more comprehensive intellectual property position for discovered materials. The need to reduce the time from discovery to deployment is driven, in part, by potential R&D cost savings for each successfully commercialized material. However, the major incentive for accelerating the pace of discovery to deployment is the ability to capitalize on the innovations at a much earlier date.

## 5. Catalyst technology—examples

Three examples serve to demonstrate the process of materials innovation, development, and commercialization to meet ExxonMobil's needs for improved product quality. The first is the development of advanced dewaxing catalysts. Catalytic hydroisomerization improves lubricant and distillate fuel viscometrics by selectively restructuring long chain alkanes to have branches periodically along their backbone. Over the past 15 years, ExxonMobil has utilized its capability to discover and develop novel microporous materials along with its understanding of supported metals and metal placement to innovate in this area. Today, it has developed several generations of lube and diesel dewaxing catalysts that the company both uses internally and licenses to other refiners.

MSDW-2 represents the latest in the development of lubricant hydroisomerization technology. The technology uses a special proprietary catalyst to very selectively place side chains on the longer lube-range paraffins. Yields and viscometrics (e.g., viscosity index or VI) are significantly better than conventional solvent dewaxing and greatly improved over the first generation, MSDW-1 catalyst (Fig. 4).

The second example involves a class of supported metal catalysts that are used for removing sulfur from catalytically cracked gasoline. SCANfining [4] is ExxonMobil's proprietary technology for the production of low-sulfur gasoline The process uses a specially designed supported metal catalyst, commercialized with Akzo Nobel Catalysts (now Albemarle Catalysts) that selectively converts mercaptans and thiophenes with minimal saturation of the gasoline-range (mainly C5 and C6) olefins which contribute significantly to gasoline octane. The design basis for the catalyst emerged from the company's firm understanding of supported metals and control of the metal function.

Fig. 5 shows some of the performance data for SCANfining. The graph on the left plots product sulfur

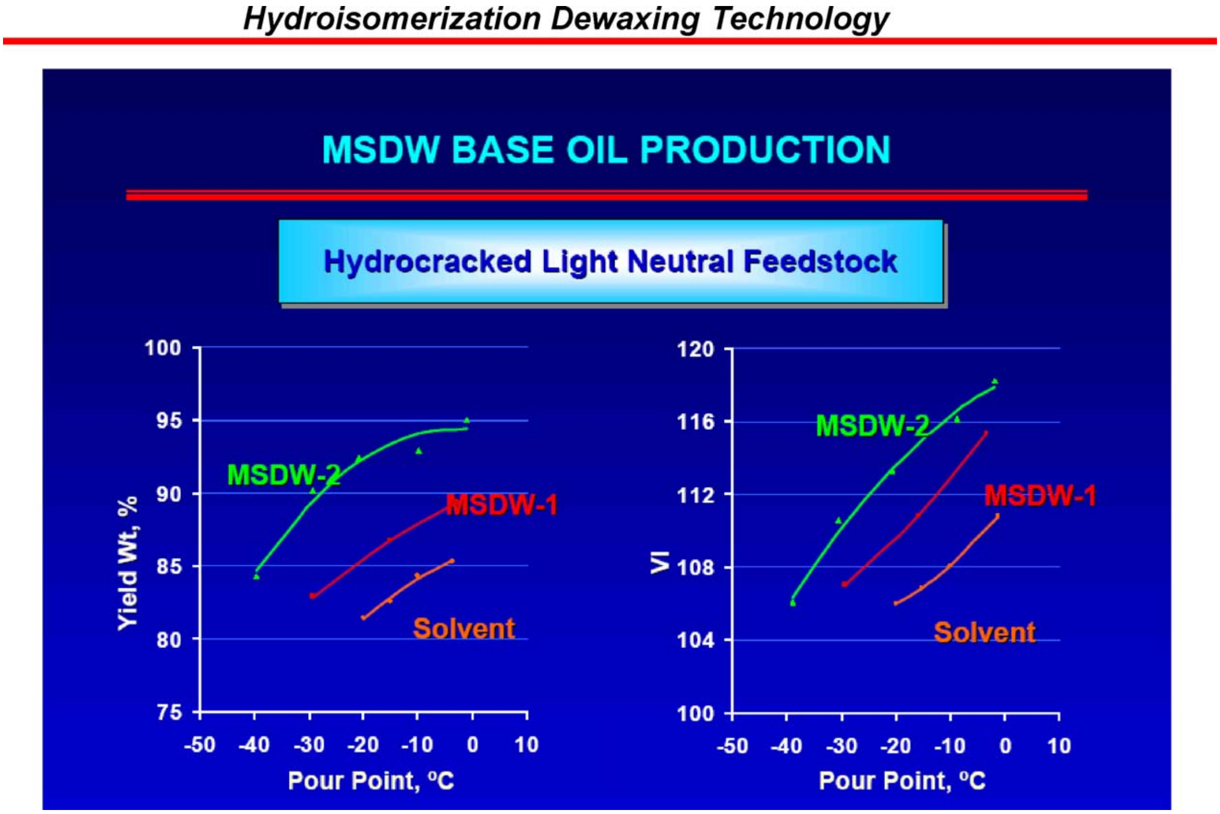


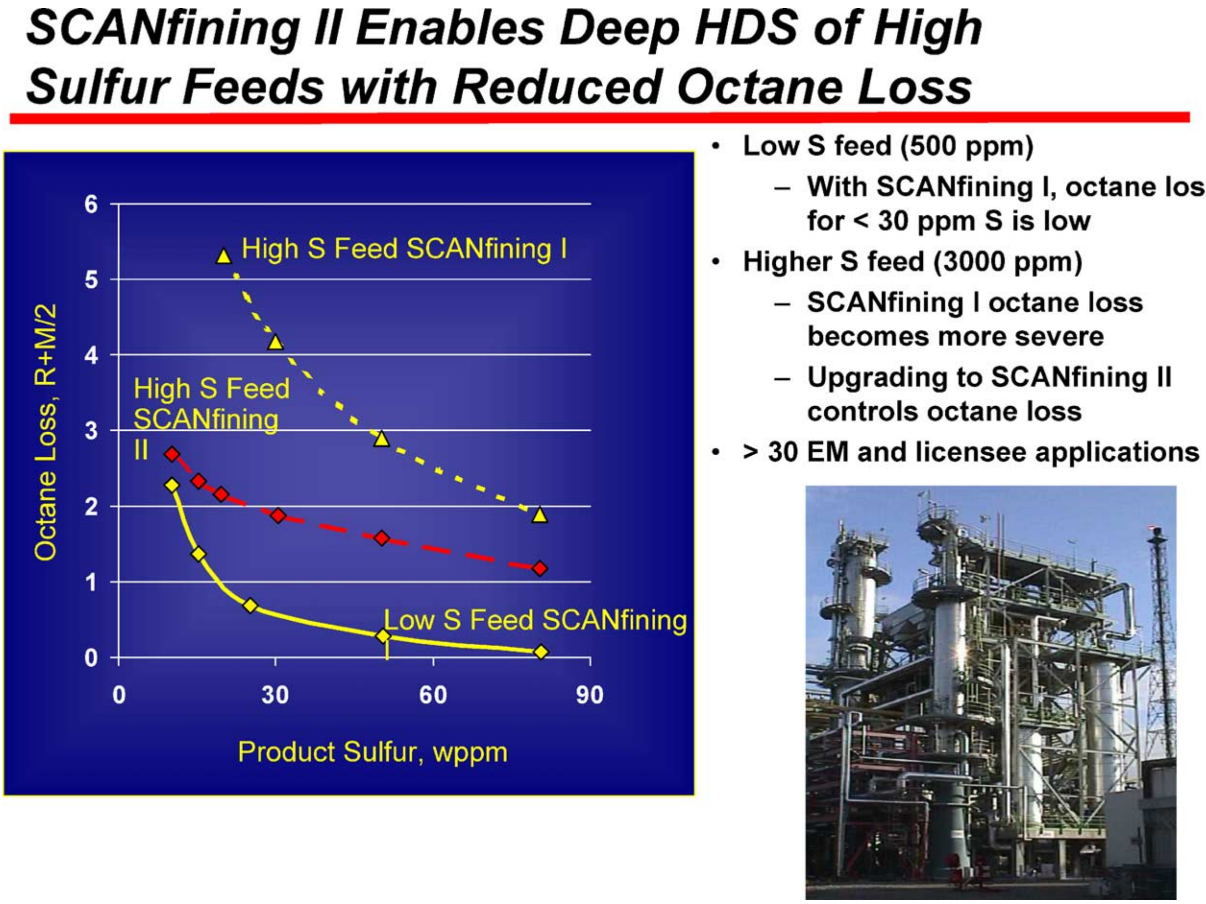
Fig. 4. Hydroisomerization dewaxing technology; two generations of lubes hydroisomerization processes – MSDW-1 and MSDW-2 – comparison with solvent dewaxing.

(in ppm) versus octane loss. For relatively low sulfur feed gasolines, the first generation SCANfining technology shows very low octane loss or hydrogenation of olefins for product sulfur targets of less than 30 ppm. However, if the feed sulfur is significantly higher, for example, 3000 ppm, the octane loss increases because more olefins are hydrogenated when the process is driven to achieve the same product sulfur level.

ExxonMobil has developed a second generation SCANfining technology, SCANfining II that shows even greater improvement in limiting octane loss. For the same high sulfur feed, the octane loss is very similar to the octane loss at very low sulfur levels. This technology is rapidly becoming the technology of choice for the production of low sulfur gasoline. Over 30 units are either announced or in operation. SCANfining capacity is expected to exceed more than 950,000 barrels per day over the next several years.

As US sulfur requirements for on-road diesel move toward 30 ppm by 2006, and 10 ppm by 2010, the removal of so-called ‘‘hard sulfur’’ species such as di-beta substituted dibenzothiophenes will become essential. Because of the steric hinderance of the alkyl groups adjacent to the sulfur atom, the desulfurization reaction rate is reduced. Kinetic studies have demonstrated that the disubstituted dibenzothiophenes (DBT) are 30–50 times less reactive than unsubstituted dibenzothiophene (Fig. 6). Some recent approaches to addressing the problem include isomerization of the alkyl groups into positions where they have less of a steric hindrance and selective hydrogenation of one of the aromatic rings to allow the molecule to flex more and therefore become non-planar. The objective of both of these approaches is to allow the molecule to have greater access to the active catalytic site. Recent studies have also shown that nitrogen compounds, both basic and non-basic, can have a significant effect on desulfurization of molecules such as DBT because they selectively adsorb on the same sites active for desulfurization. Thus, research has focused on the investigation of structure–reactivity relationships of more advanced catalysts to optimize sites that can attack not only ‘hard sulfur’ species but ‘hard nitrogen’ species as well.

The third example involves a truly breakthrough hydroprocessing catalyst for removing sulfur from distillate stocks. Fig. 7 plots the relative activity of distillate hydrodesulfurization catalysts as a function of time. Until the last 4 years improvements have been relatively incremental. However, over the past several years there have been significant developments. A real breakthrough in hydrodesulfurization catalyst technology has been the development of Nebula catalysts. The technology was discovered by ExxonMobil in the last decade and was recently commercialized jointly with Albemarle Catalysts. Nebula is a unique composition that differs substantially from traditional hydroprocessing catalysts based on combinations of metals deposited on a high surface area support.



**SCANfining II Enables Deep HDS of High Sulfur Feeds with Reduced Octane Loss**

- Low S feed (500 ppm)
  - With SCANfining I, octane loss for < 30 ppm S is low
- Higher S feed (3000 ppm)
  - SCANfining I octane loss becomes more severe
  - Upgrading to SCANfining II controls octane loss
- > 30 EM and licensee applications

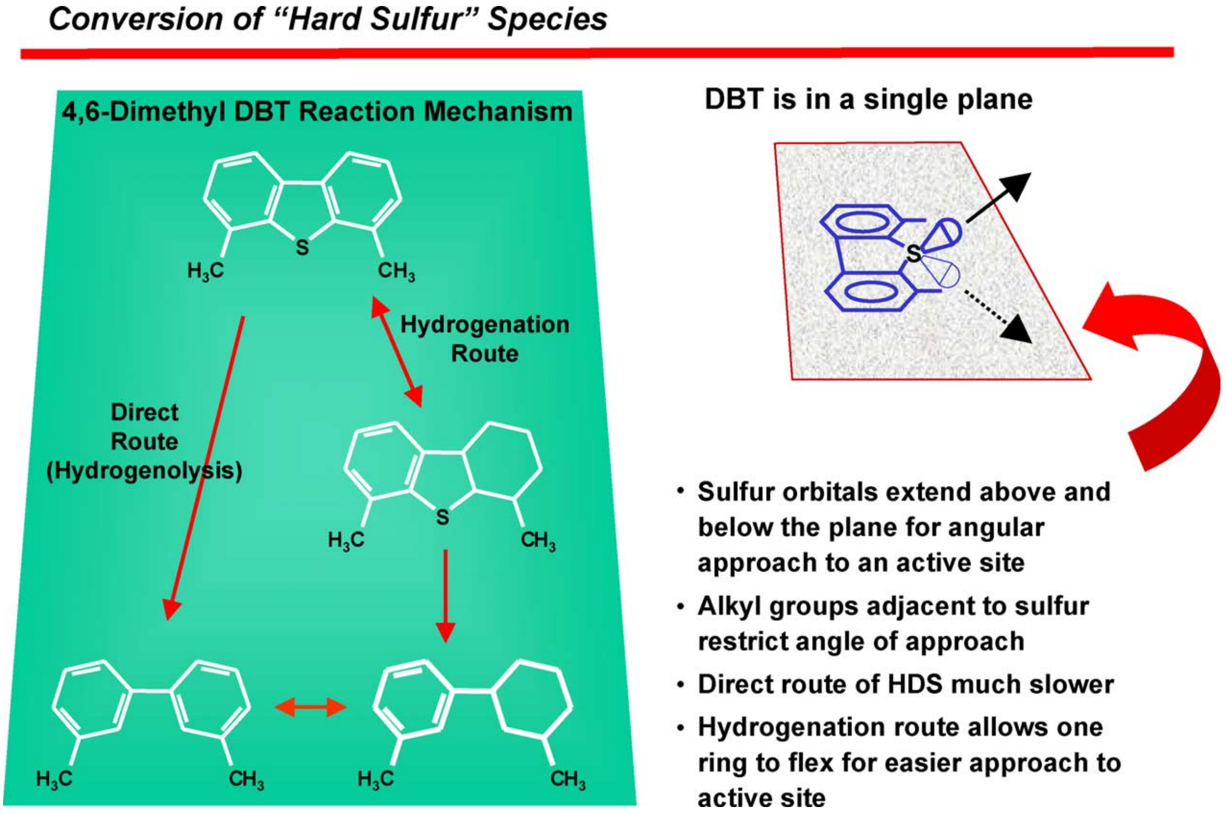
Fig. 5. SCANfining II enables deep HDS of high sulfur feeds with reduced octane loss.

The activity of Nebula is at least three times greater than that of earlier hydroprocessing catalysts. Because of its unique composition, producing a finished Nebula catalyst presented a challenge to developers. This challenge was successfully overcome through the combined efforts of ExxonMobil researchers and scale-up and commercialization expertise brought by Albemarle. The Nebula catalyst has been successfully commercialized for a number of applications including ultra-low sulfur diesel fuels [5] and distillate hydrocracking [6]. Like the previous catalyst used in SCANfining, ExxonMobil uses Nebula internally. The significantly enhanced activity of the Nebula catalyst allows a “drop-in” solution into existing units without having to spend capital to build additional units or increase the operating pressure of hydrodesulfurization units.

In each of these three examples, the development of step-out catalysts drew heavily from existing materials platforms. Fundamental understanding of the material structure–function relationships provided a strong base around which the catalysts were developed. An understanding of the complexities associated with the scale-up steps allowed developers to anticipate and adequately address manufacturing problems. However, in all but one of the cases, the time required to move from initial concept to full-scale manufacture was protracted. In fact, the norm in taking truly novel material from the discovery through the commercialization stage is on the order of 5–10 years. Efforts to reduce the time required to move new materials through the system are now focused on accelerated discovery and development work processes assisted by high throughput experimentation (HTE).

## 6. High throughput experimentation

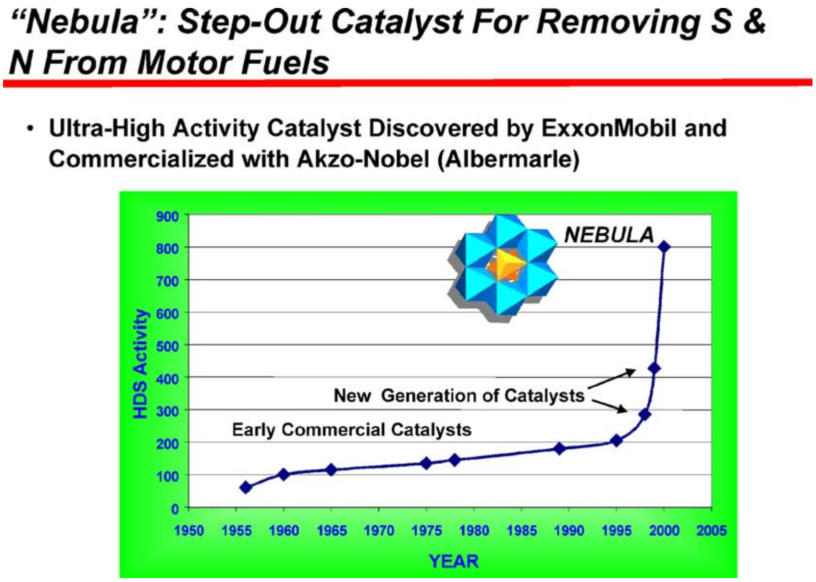
Attempts to conduct massively parallel or very rapid sequential experimentation to improve research productivity initially started in the pharmaceutical area and then spread to the fine chemicals and polymers areas. Recently, high throughput experimentation capabilities have begun to appear in petrochemical and refining R&D laboratories. These capabilities constitute a suite of technologies that accelerate not only the pace of discovery, but also the pace of process and materials development by providing a broader and richer knowledge base which reduces the risk of skipping steps along the process or materials development pipeline. High throughput tools are integrated into ‘workflows’, which comprise sequential materials synthesis, characterization, and materials performance evaluation steps. Workflows are typically highly instrumented and



**Conversion of "Hard Sulfur" Species**

- Sulfur orbitals extend above and below the plane for angular approach to an active site
- Alkyl groups adjacent to sulfur restrict angle of approach
- Direct route of HDS much slower
- Hydrogenation route allows one ring to flex for easier approach to active site

Fig. 6. Conversion of "hard sulfur" species.



**"Nebula": Step-Out Catalyst For Removing S & N From Motor Fuels**

- Ultra-High Activity Catalyst Discovered by ExxonMobil and Commercialized with Akzo-Nobel (Albermarle)

Fig. 7. "Nebula": step-out catalyst for removing S & N from motor fuels.

are constructed around robotics and miniaturized experimentation. Conceptually, high throughput technologies may also link with process modeling so that the small-scale experiments can be effectively linked to larger pilot plants and eventually commercial units. A critical component in the collection and interpretation of the massive amounts of data is an informatics system, which allows the data to be rapidly accessed and processed through advanced visualization software and methods such as principal component analysis. In essence, high throughput technologies provide an ability to carry out a larger number of experiments with correspondingly increased prospects for discovery. Used correctly, these techniques accelerate the identification of leads, reduce the cost per experiment, and progress development programs more rapidly.

In July of 2003, ExxonMobil and Symyx Technologies, Inc., a pioneer and leader in the development and application of high-speed materials research methods, announced a technology alliance focused on high throughput experimentation. This alliance is representative of ExxonMobil's commitment to innovation and technology and recognizes the commercial value of HTE.

ExxonMobil's agreement with Symyx marks a very extensive and highly integrated commitment to apply HTE technology across its entire downstream and chemical portfolio. Under the terms of the agreement, the companies will work together over a 5-year period in a number of fields seeking faster paced development of chemicals, lubricants, and fuels products and processes to continue to expand markets and meet customers' changing needs.

The tools and techniques developed as part of this alliance will enable ExxonMobil to generate new products and accelerate the commercialization of new technologies, broadening ExxonMobil's intellectual property portfolio.

Fig. 8 shows an example of an integrated high throughput workflow for catalyst synthesis, characterization and performance evaluation. The picture at top left shows an automated high-speed robotic device that combines the appropriate catalyst components. This is followed by a series of synthesis and formulation steps where the active materials are synthesized, binding and support materials are added, and metals are impregnated onto supports. After the catalysts are prepared they are automatically transferred to a primary screening test, shown here as a set of small wells. The objective of this step is to rapidly scan the materials in order to identify a single performance parameter, such as activity. As promising candidates are identified, the focus turns to the use of secondary tools where catalysts can be evaluated in parallel on a larger scale for a more extensive set of performance parameters. This step is geared toward obtaining information critical to the selection of the best material for the application. Scale-up of the catalyst involves the addition of binders, various modifiers, or metal salts. Larger pilot plants are used to validate the results derived from the smaller scale HT equipment, to produce sufficient quantities of product for performance evaluation, and occasionally, to study the longer term stability of the preferred catalyst. The data from all of the evaluations are used to refine the catalyst formulation prior to commercialization. An informatics system collects the data, facilitates the design of further experiments, and aids in the visual interpretation of the data. Significant advantages can be realized using an informatics suite that enables data collection and analysis across each of the various research

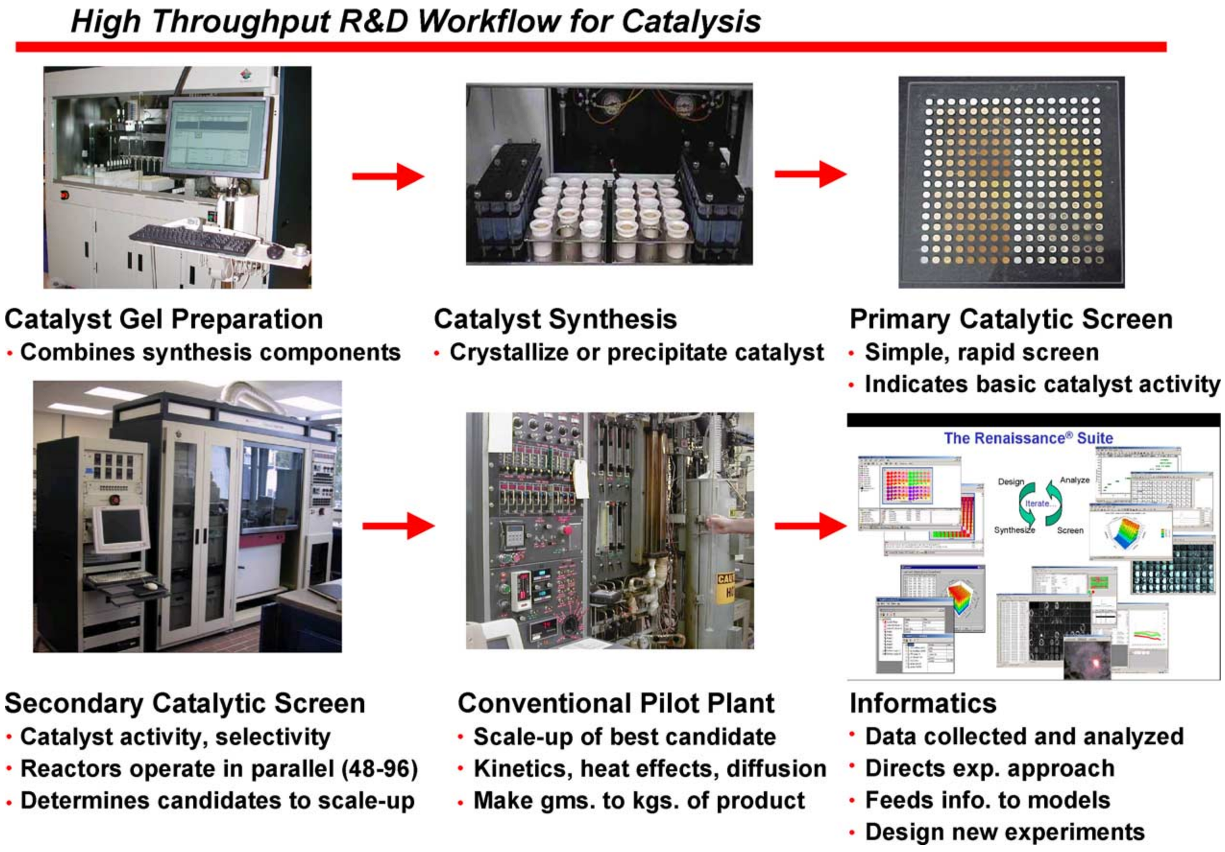


Fig. 8. High throughput R&D workflow for catalysis.

stages for a particular project—primary synthesis and screening, secondary synthesis and screening, and pilot plant synthesis and screening.

## 7. Conclusions

Driven by more stringent fuel, lubricant, and chemical product specifications and poorer quality feedstocks, the refining and petrochemical industries have come to rely even more heavily on development of new catalytic technology. ExxonMobil, a beneficiary of the merger of two strong and complementary catalytic technology organizations, has focused developing materials platforms, which promote innovation of new process technologies. Efforts to accelerate the development of new catalytic technology have been augmented by the establishment of an alliance aimed at the use of high throughput technologies to reduce the time between discovery and commercialization.

## References

[1] T.G. Kaufmann, A. Kaldor, G.F. Stuntz, M.C. Kerby, L.L. Ansell, Catal. Today 62 (2000) 77.
[2] Diesel World, October 31, 2004. p. 2.
[3] Department of Energy, Energy Information Administration, 2003.
[4] K.L. Riley, J.L. Kaufman, S. Zaczepinski, P.H. Desai, S.W. Mayo, Akzo Nobel Catalyst Symposium, vol. G-3, 1998, p. 1.
[5] T. Reid, K. Kunz, S. Mayo, AM-04-55, off-setting the cost of ultra low sulfur diesel, in: 2004 NPRA Annual Meeting, San Antonio, 2004.
[6] G. Meijburg, E. Brevoord, F. Plantenga, S. Mayo, Y. Inoue, K. Fujita, W. Lewis, A. Sapre, NEBULA$^{TM}$ for Hydrocracker Pretreat Operations, ERTC, London, 2003.